

Cyclization of diols with ammonia over CuO—ZnO—Al₂O₃ catalyst in the presence of H₂

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Cyclization of diols with ammonia in an H₂ atmosphere over an industrial CuO—ZnO—Al₂O₃ catalyst for the synthesis of methanol (SNM-1) gives nitrogen-containing five-, six-, or seven-membered heterocyclic compounds. The yields of cyclic amines in the 180–230 °C temperature range are 46 to 97 %.

Key words: diols, ammonia, cyclization, heterocyclic amines, copper-containing catalyst.

Cyclization of diols with ammonia holds a firm place among methods for the synthesis of nitrogen-containing heterocyclic compounds.¹

Synthetic potentialities of this reaction can be substantially increased by using heterogeneous catalysts that are normally employed for amination of alcohols.^{2,3} For example, a number of papers have dealt with the synthesis of pyrrolidine from 1,4-butanediol and ammonia in the presence of oxide^{4,5} or metal^{6,7} catalysts. However, with these catalysts, the yield of pyrrolidine was not very high; at best, it amounted to ~70 % (see Ref. 6).

Cu-containing systems² and industrial catalysts for the synthesis of methanol^{8,9} are among the most active heterogeneous catalysts of amination of alcohols. The properties of Cu-containing catalysts in cyclization of diols have not been studied. It has only been reported that these catalysts exhibit high activities in intramolecular amination of amino alcohols giving cyclic amines.^{10,11}

The purpose of the present work is to study the possibility of direct one-step synthesis of nitrogen-containing heterocyclic compounds from diols and ammonia in the presence of the industrial catalyst of the synthesis of methanol.

Experimental

The reaction of diols with ammonia was carried out in the presence of hydrogen in a steel tubular flow reactor with a fixed bed of SNM-1 industrial catalyst (consisting of (wt. %) 52–54 CuO, 24–28 ZnO, 5–6 Al₂O₃).¹² Hydrogen present in the reaction zone not only served as the carrier gas for the reactants and reaction products, but also ensured the stability of the catalyst during the synthesis. The hydrogen–ammonia mixture was prepared by passing H₂ through a temperature-controlled bubbler with liquid NH₃. The proportion of ammonia

in the initial gas mixture was controlled by varying the temperature of the bubbler.

The reaction was conducted under the following conditions: $T = 160$ to 230 °C, $p_{\text{NH}_3} = 0.85$ MPa, $p = 3.5$ MPa, volume rate of H₂ (v_{H_2}) 2000 h^{-1} , feed rate of diol (v_d) $2.2 \text{ mol h}^{-1} \cdot (\text{L Cat})^{-1}$. All of the starting diols, 2,3-butanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, and 1,10-decanediol, were of 98–99 % purity. The ammonia and hydrogen with purities higher than 99.9 %, used in the experiments were taken from cylinders. Diols were introduced into the reactor using a dosing apparatus (the accuracy of the introduction was ± 5 %) as THF solutions; 1,6-hexanediol and 1,10-decanediol were introduced as solutions in *tert*-butyl alcohol. We previously showed that these solvents do not react with ammonia or hydrogen.

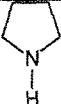
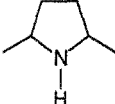
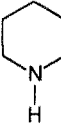

Prior to the use in the synthesis the catalyst was reduced with hydrogen for 6 h at 250 °C at a pressure of 3.5 MPa.

The reaction products and recovered reactants leaving the reactor were condensed in two successively connected separating traps, cooled to 20 and 0 °C. The products were analyzed by GLC using a Chrom-5 chromatograph with a flame ionization detector, a 1200×3 mm column packed with 5% Carbowax 20M + 3 % KOH + 0.5% Apiezon M on Chromosorb G (60/80 mesh), and N₂ at a flow rate of 50 mL min^{-1} as the carrier gas. Temperature-programming: 50–230 °C, 10–20 °C min^{−1}. The reaction products were identified by GC–MS (the chromatography was carried out under the same conditions) on a KRATOS-MS 25RF/DS-90 instrument at an energy of ionizing electrons of 70 eV, an emission current of 50 μA , and a temperature of the ion source and molecular separator of 200 °C.

Results and Discussion

We found that cyclization of diols with ammonia in the presence of hydrogen and SNM-1 catalyst occurs in the case of 1,4-butanediol, 2,5-hexanediol, 1,5-pentane-

Table 1. Cyclization of diols with ammonia in the presence of SNM-1 catalyst

Starting diol	Expected amine	Temperature/°C	Yield of amine (%)	Mass spectrum of amine*, m/z (I_{rel} (%))
1,4-Butanediol		180 200 220	1 52 94	72(9), 71 [M^+] (72), 70(80), 69(10), 68(23), 44(19), 43(100), 42(70), 41(72), 40(20), 39(59), 38(10), 30(46)
2,5-Hexanediol		160 180 220	48 97 95	99 [M^+] (10), 98(16), 85(10), 84(100), 72(8), 71(28), 70(14), 55(8), 45(6), 44(29), 43(21), 42(64), 41(38), 39(21), 30(16)
1,5-Pentanediol		180 200 220 230	38 46 81 94	85 [M^+] (76), 84(100), 71(12), 70(25), 69(10), 68(8), 67(9), 58(13), 57(80), 56(92), 55(29), 54(12), 53(8), 51(6), 44(73), 43(58), 42(79), 41(32), 40(8), 39(34), 30(65)
1,6-Hexanediol		180 200 220 230	8 37 92 97	100(12), 99 [M^+] (53), 98(23), 84(12), 71(10), 70(98), 68(7), 57(50), 56(65), 55(11), 44(43), 43(100), 42(34), 41(35), 39(22)

Note. Cyclization conditions: $p_{tot} = 3.5$ MPa, $p_{NH_3} = 0.85$ MPa, $v_d = 2.2$ mol $h^{-1} \cdot (L \text{ Cat})^{-1}$, $v_{H_2} = 2000$ h^{-1} , NH_3 : diol = 10 : 15).

* Characteristic ions in the mass spectra, m/z (intensities in % of the maximum peak intensity, peaks with intensities of less than 5 % are not presented).

diol, and 1,6-hexanediol (Table 1). The synthesis yields five-, six-, or seven-membered saturated nitrogen-containing heterocyclic compounds: pyrrolidine, 2,5-dimethylpyrrolidine, piperidine, and hexamethylenimine, respectively. The highest yields of cyclic amines (81–97 %) were observed at 220–230 °C. In addition to cyclic unsubstituted amines and the recovered diols, the reaction products contained minor quantities (up to 10 %) of *N*-substituted amines. Attempts to prepare three-, four-, or eleven-membered cyclic amines were unsuccessful. To elucidate probable reasons why these heterocyclic amines are not found in the cyclization products, a special study is required. Now we may suppose only that five-, six-, and seven-membered saturated cyclic amines are the most stable under the conditions chosen for the experiments.

Thus, the use of SNM-1 catalyst for cyclization of diols with ammonia makes it possible to prepare pyrrolidine, its *C*-alkylated derivatives, piperidine, and hexamethylenimine in high yields.

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